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Influence of monomer architecture on the shear properties of molecularly thin polymer melts

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The effective viscosity and shear behavior of ultrathin films of two structurally different perfluoropolyether fluids have been investigated. The materials used were Fomblin Z, a linear random copolymer of fluoroethylene oxide and fluoromethylene oxide, and Fomblin Y, a branched random copolymer with fluoropropylene oxide and fluoromethylene oxide monomer units. The shearing experiments were conducted with the fluids confined between molecularly smooth surfaces at shear rates ranging from 200 to $4 \times 10^3 \text{ s}^{-1}$. It was found that when the thickness of the fluid films decreases from 10 to 2 nm, both perfluoropolyethers exhibited a sharp increase in viscosity, from bulk values to "surface viscosity" values that are many orders of magnitude larger. With increasing shear rates, the Z-type fluid showed a gradual decrease in the shear stress indicating an apparent ordering of the molecules due to the applied shear forces. On the other hand, with the Y-type copolymer, the shear stresses were significantly lower and were proportional to the shear rate resembling Newtonian fluids. The results are explained in terms of the differences in the molecular architecture of the fluids and suggest a close relation between the molecular structure of the polymer melt near a solid wall and its frictional and lubricating properties.

I. INTRODUCTION

Many applications of polymeric materials depend on how well one understands the response of polymers during mechanical deformation such as compression or shear. A knowledge of the influence of the dynamic loading on the interfacial properties of monomolecular and thin polymer films is important for understanding and controlling many different lubricating processes. Ideally one strives for understanding of these processes at a molecular level as demonstrated in the early experiments conducted in the Cavendish Laboratory by Tabor and many of his co-workers.^{1,2} The emphasis was on the understanding of the frictional properties of close packed Langmuir-Blodgett monolayers deposited on atomically smooth mica substrates. A systematic study of the effects of temperature, sliding velocity and contact pressure upon the interfacial strength of a number of carboxylic acids and some of their soaps, as well as fluorinated analogous, was carried out.³ The results implied that shear is accommodated by the simultaneous movement of several chain ends in the plane of shear and supported the proposed dislocation model, which links the shear properties of the monolayers to their compressibility. With thicker and relatively unstructured multilayers the shear was different and reportedly due to the orientability of the alkyl chains in the direction of shear.

The importance of polymer orientation processes in friction was subsequently shown in several other studies with semicrystalline and glassy polymer films.^{4,5} Diffraction studies⁶ confirmed that polymers which exhibit initially high friction followed by lower friction values are highly oriented under shear, with molecules aligned in the direction of sliding. Examples of these materials are perfluorotetrafluoroethylene (PTFE) and high density polyethylenes (also termed "smooth molecular profile" poly-

mers by Pooley and Tabor⁴). They also showed that the inclusion of side groups such as $-\text{CF}_3$ along the backbone of the molecule appears to hinder the translational motion of the polymer chains in relation to each other resulting in an increase in friction that is proportional to the branch content.

The influence of processing (shear induced polymer alignment), morphology, and molecular topology on the mechanical properties of bulk polymers has indeed been recognized for a long time.⁷⁻⁹ A broad range of properties can in fact be obtained by simply varying the branch characteristics.^{10,11} For example, Brady and Thomas,¹² in their recent work with branched linear polyethylene films, demonstrated that variation in the branch content and distribution has a pronounced effect on the crystallinity of the film and consequently on its melting behavior.

In polymer melts, molecular topology plays a similar role which, perhaps is best illustrated by the shear behavior of methylpolysiloxanes fluids.¹³ At low molecular weights (viscosity below 1000 cp), these fluids exhibit Newtonian behavior, that is the shear stress is proportional to the shear rate. With increasing chain length, the polymer begins to show pseudoelastic properties, and the viscosity shows a deviation from linearity, which grows larger with increasing molecular weight. The accepted explanation of this behavior is as follows: At rest, with viscosity of the polymer at a maximum, the melt is composed of long and linear molecules in various states of entanglement and orientation. At low shear rates, the tendency of the molecules to align in the direction of shear is negligible and the fluids are Newtonian. However, with increasing shear rates, the molecules begin to order showing a typical shear thinning behavior. As the molecular weight increases, chain entanglement and molecular disorder are initially larger leading

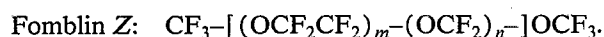
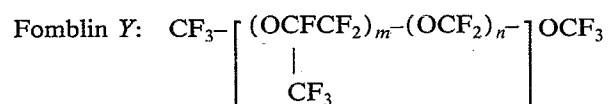
to increasingly larger differences in the resistance to shear between low and high shear rates.

In many practical applications, especially when molecularly thin polymeric melts are used as lubricants, rheological properties of these films are simply unknown. Recently, application of the surface force apparatus to measurements of shear behavior of molecularly thin organic films¹⁴⁻¹⁹ allows for a better understanding of the transition regime which links bulk and surface properties. In these experiments, simple hydrocarbon liquids with film thicknesses ranging from 5–50 Å were sheared between atomically smooth mica surfaces. In response to shear, liquids in excess of 50 Å in thickness showed a typical viscous response. As the thickness decreased with applied load, the dynamic friction was shown to be "quantized" according to the number of layers of molecules between the mica surfaces.¹⁴ With one or two layers separating the surfaces, the film exhibits solid-like behavior with a yield stress of several orders of magnitude in excess of the bulk viscosity. It was also shown that with longer molecular chains, e.g., tetradecane, the molecules tend to order in response to the applied shear and to relax following a pause in sliding.^{16,17} Introduction of side groups such as CH₃ along the hydrocarbon chain (2-methyloctadecane) was noted to smear the quantization of friction and also decrease the tendency of the molecules to align in the shear field.¹⁷

The purpose of this paper is to extend the previous studies with low molecular weight hydrocarbons to economically important class of high molecular weight perfluoropolyethers. These materials are currently almost exclusively employed in the computer industry as lubricants for rigid magnetic disks.²⁰ Due to the operating conditions, the thickness of these lubricating films must be kept to a minimum and is usually in the range of 10–50 Å. It is our objective to shed some light on the rheological properties of these molecularly thin lubricating fluids by comparing the behavior of a linear copolymer, with molecularly even structure, to a chemically similar polymer where the regularity of the chain is perturbed by –CF₃ side groups.

II. MATERIALS

Perfluoropolyether (PFPE) fluids are frequently used as lubricants because they show many desirable properties, such as low surface tension, high chemical stability, thermal and oxidative resistance, and excellent lubricity. In this work, two types of PFPE fluids²¹ were investigated:



Both materials are random copolymers. From nuclear magnetic resonance (NMR) measurements^{22,23} it was found that in Fomblin Y, $m \gg n$, while in the Fomblin Z, m represents approximately 40% of the groups and n 60%. Experiments were carried out on one fraction of each type of PFPE:

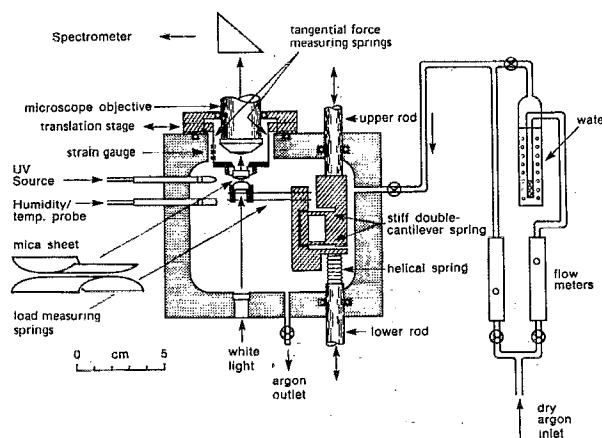


FIG. 1. Schematic drawing of the Shearing Force Apparatus outfitted with a translational stage. The lateral sliding mechanism permits two surfaces to be sheared past each other at various sliding speeds while simultaneously controlling the normal load and measuring the transverse force. The environment is maintained by purging the instrument with argon at the flow rate of 2 cc/min.

Type Y: $M_n=6830$, $M_w=9060$,

Type Z: $M_n=12\,800$, $M_w=16\,800$.

The bulk viscosities were determined on a Ferranti-Shirley cone and plate viscometer at 25 °C operating temperature.²⁴ Both fluids were used as received following overnight centrifugation at 16 000 rpm. This step was essential to remove any solid or gel-like particles potentially harmful in the sliding experiments. The 1:1 blend of Y and Z type polymers by weight was prepared by dissolving the fluids in Freon TF (1,1,2-trichloro-1,2,2-trifluoroethane) and subsequently removing the solvent by evaporation under vacuum.

III. EXPERIMENT

The experiments reported here make use of an apparatus that is primarily used for measuring equilibrium or static interface forces in liquids and vapors.²⁵ The technique is capable of directly measuring the force between two curved, molecularly smooth mica surfaces as a function of their separation. The mica substrate is silvered on the back side and two such surfaces, opposing each other in a cross-cylinder configuration, form a symmetric three-layer interferometer which allows the surface separation to be determined to within about 0.1 nm with multiple-beam interferometry.²⁶ The contact area between the molecularly smooth surfaces can be determined from the shape of the interference fringes. Changes may be readily observed, in real time, by monitoring the changing shapes of these fringes.

For the friction measurements a sliding attachment, already described elsewhere, was used.¹⁴ As shown in Fig. 1, the upper surface is mounted at the lower end of two parallel vertical springs, one of which acts as a frictional force detector by having strain gauges attached to it. The lateral sliding mechanism permits two surfaces to be

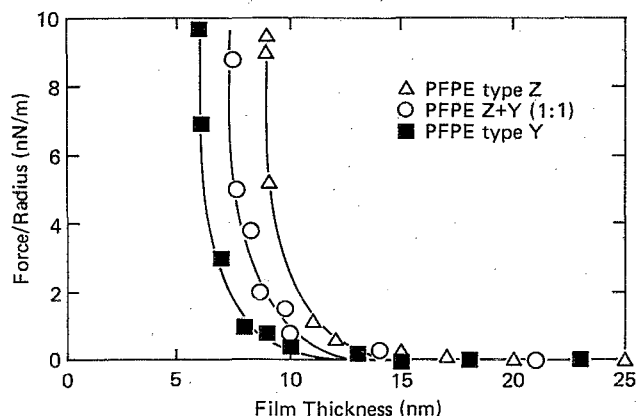


FIG. 2. Measured forces between mica surfaces separated by perfluoropolyether fluids. When compressed under a very large force the two surfaces flatten but do not come any closer than shown by the arrows (referred to as "hard wall"). This hard wall corresponds to a compressed polymer layer at each surface and is equal to 6.4 nm for Y, 7.4 nm for Z + Y blend, and 9 nm for Z type polymers, respectively.

sheared past each other at various sliding speeds while simultaneously controlling the normal load and measuring the transverse force. The sliding was carried out under loads varying from 2.5 to 25 grams, with sliding velocities ranging from 1 to 10 $\mu\text{m}/\text{sec}$. The environment was controlled by continuously purging the instrument with 99.999% pure argon at the flow rate of 2 cc/min. Two hours were allowed for the system to equilibrate prior to measurements.

IV. RESULTS

A. Equilibrium forces

Several separate experiments were performed using new, i.e., freshly cleaved, mica for each experiment. Initially, the surface were brought together in dry argon to establish the "contact position," $D = 0$, and to ascertain that there were no dust particles and that true molecular contact has been obtained. Prior to the measurement, the surfaces were separated and a 0.1–0.3 ml drop of PFPE fluid was injected between them. The surfaces were then brought together and the normal forces at specific surface separations were measured. Changes in the separation distance were made stepwise with an equilibration time of 3 min. for each step.

Figure 2 shows the force vs distance results for the two PFPE fluids. A monotonic repulsive force was observed at separations below 14 nm for type Z, 11 nm for type Y, and 12.3 nm for the Y + Z blend, which increased steadily with decreasing separation. The decay lengths are 1.3 and 1.5 nm for the Y and Z polymers, respectively. The position of the hard wall appears to scale with molecular weight of the sample, with 9 nm for Fomblin Z and 6 nm for lower molecular weight Fomblin Y. An intermediate thickness, ~ 7.2 nm, was measured for the 1:1 blend of the polymers.

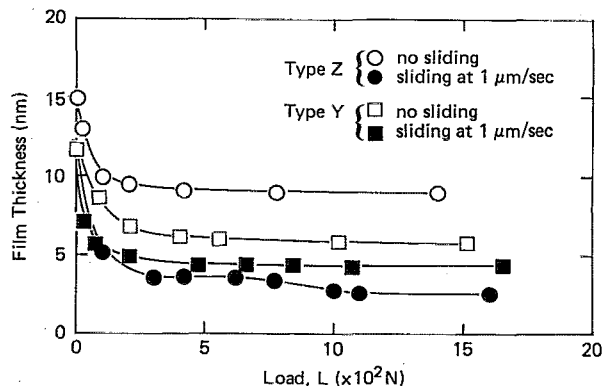


FIG. 3. Measured film thickness vs load. Bottom two curves show respective behavior of polymers Y and Z during sliding. The equilibrium forces for the polymer Y and Z (upper curves) are included to highlight the effect of shear on the film thickness.

B. Shear behavior

1. The effect of load at constant velocity

In the compressive experiments, the position of the hard wall was not affected by application of loads as high as 25 grams. With a typical contact area of $1 \times 10^{-4} \text{ cm}^2$, this translates to a compressive pressure of 250 atmospheres. In the dynamic situation, however, when tangential shear and normal loads acted upon the film, the thickness of the hard wall decreased very rapidly as shown in Fig. 3. Even under a moderate load of 2.5 grams, the reduction in thickness was significant. At larger loads, the thickness of the branched polymer (Y type) levels off to an asymptotic value while that of the linear polymer (Z type) continues to decrease in a stepwise fashion, with step heights on the order of 0.8 nm.

2. The effect of shear rate at constant load

Figure 4 shows the results for shearing PFPE fluids at a constant load and the dynamic thickness of the respective

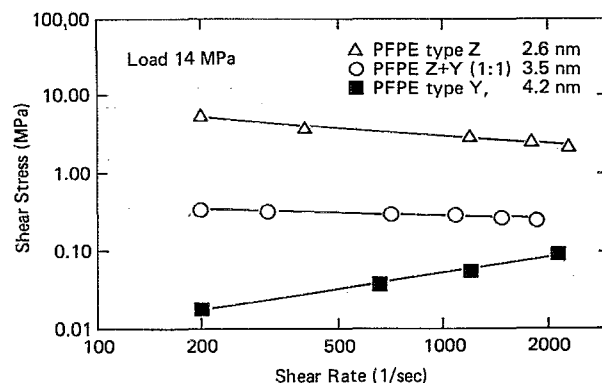


FIG. 4. Shear stress vs shear rate. Shearing of the Z type fluid results in decreasing shear stress with sliding velocity while the opposite holds for the Y type. The 1:1 blend of Z and Y shows an intermediate behavior. It should be noted that the load and thickness were held constant throughout the experiment.

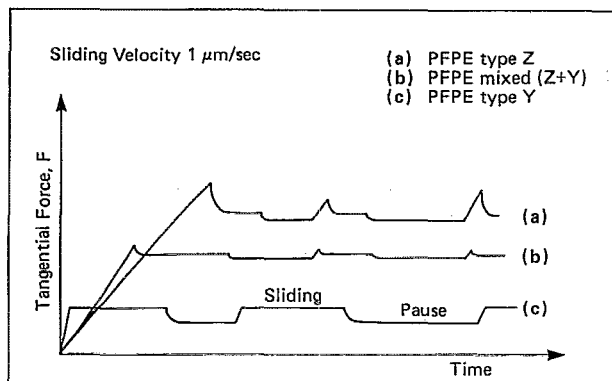


FIG. 5. Schematic drawings of some typical chart-recorder traces, showing changes in friction during different phases of sliding. Polymer Z (a) shows a considerable static friction followed by a lower value of dynamic friction. Interruptions in sliding result in frictional peaks with their magnitude depending on the rest time. The bottom trace (c) represents the polymer Y exhibiting equal static and dynamic friction. The 1:1 blend (b) shows an intermediate frictional behavior.

polymers. Two features of these data are particularly interesting. First, while the bulk viscosity of the Y type polymer is almost an order of magnitude higher than the Z type, in molecularly thin films, the shear response is reversed. At all shear rates, the shear stresses are higher for latter than for the former. Second, the "effective viscosities" of these polymers are several orders of magnitude larger than their corresponding bulk values. Clearly, these fluids are drastically altered when molecules are in proximity of surfaces, and it is obvious that properties of thin films cannot be extrapolated from the bulk values.

Another salient feature of Fig. 4 is the frictional or shear stress response to the applied shear rate. With increasing shear rate, the linear polymer shows a "shear thinning" behavior as evident by the reduction in the shear stress with sliding velocity. In contrast, the Fomblin Y with $-\text{CF}_3$ side groups behaves like a Newtonian fluid with the shear stress increasing proportionally with shear rate. The 1:1 blend of the Y and Z fluids exhibits an intermediate response with a small dependence on shear rate.

An interesting aspect of the shear response to the applied shear rate is illustrated schematically in Fig. 5. The data show changes in the friction during different phases of sliding. The linear polymer shows a considerable static friction, defined as the tangential force required to initiate sliding, followed by a lower value of dynamic friction. A pause in sliding is followed by another frictional peak, with a difference between the static and dynamic friction strongly dependent on the rest time. The friction of the side-chained polymer (bottom trace) is more typical of a Newtonian fluid with the static friction equal to the dynamic friction. Again, the 1:1 blend shows intermediate characteristics.

V. DISCUSSION

In this paper we have presented experimental observations of the static and dynamic properties of molecularly

thin films of two polyperfluoroether polymers with different molecular structures: type Z, characterized by a "smooth" molecular profile, and type Y, with a pendant group ($-\text{CF}_3$) in the main chain.

For the static experiments (Fig. 2) we have measured the medium-range repulsive forces which might be best described by an exponential decay. As mentioned in Sec. IV A, the onset of repulsive forces was observed at distances on the order of $2\text{--}3 R_g$ for a waiting time of 3 min between steps. Also observed, in agreement with other investigators,²⁷⁻³⁰ was the presence of a steep repulsion (hard wall) at a surface separation approximately equal to two slightly compressed polymer monolayers. We can estimate a relative compressibility of the polymer coil by comparing the thickness of the hard wall with the measured dimensions of the free polymer coil in the melt. According to the data obtained by Cantow,³¹ the average end-to-end distance ($\langle h^2 \rangle^{1/2}$) of molecules Z and Y are 7 and 4 nm, respectively. Assuming a Gaussian coil, for which the radius of gyration (R_g) and end-to-end distance are related as $R_g^2 = \langle h^2 \rangle / 6$, we can calculate the thickness of a single polymer layer ($2R_g$) equal to 5.7 nm for sample Z and 3.3 nm for sample Y. As shown in Fig. 2, the position of the hard wall was measured at 9 nm (4.5 nm thick monolayer at each surface) which suggests a considerable compression (from 5.7 to 4.5 nm) of the molecules Z within the layer. In contrast, the more bulky and less flexible polymer Y showed little or no chain deformation with the position of the hard wall at 6.4 nm or 3.2 nm for each surface layer.

Often in polymer systems, it is assumed that the measured forces are the equilibrium forces. This is valid provided the equilibrium time allowed between successful compression steps is sufficiently long compared to the characteristic relaxation times that give rise to repulsion. For instance, when steric forces are present, the relatively long time required for the rearrangement of polymeric chains may lead to visco-elastic effects which are absent in true equilibrium force measurements. In polymer melts, the effect of the wall on the chain configuration is expected to persist over a distance comparable to the segment size³² and in the absence of any steric or entropic effects, it is difficult to understand theoretically the origin of these forces. Very general considerations³³ suggest the absence of strong static forces with a range $\sim R_g$ in thin films of polymeric melts. Strong evidence for this has also been provided by recent molecular dynamics simulation.³² Therefore, we are forced to conclude that the measured forces are viscous in nature and result from incomplete equilibration between successive compression steps (the experimental evidence supporting this conclusion is given in Ref. 28). However, when the polymer was strongly compressed and the surfaces were separated by the repulsive hard wall, there was no measurable change in the film thickness following overnight compression. It is conceivable that the "hard wall" also is viscous in nature but the effective viscosity is too high for an equilibrium to be reached in a reasonable time. An alternative explanation is that the polymer chains are "pinned" on the mica surface, possibly

because of epitaxial crystallization of the first segment layers adjacent to the solid, and under these circumstances the equilibrium hard wall (i.e., $\sim R_g$) is expected to exist.

The slower drainage of the polymer in thin films is consistent with the notion that the resistance to shear flow, as manifested by a restricted motion of chains in a direction normal and tangential to the surface, increases sharply within a few molecular layers to a solid surface. The constraints imposed on the mobility of the molecules by the surfaces, as well as the presence of other molecules, result in increasing viscosity with decreasing surface separation. Recently, Chan and Horn,³⁴ as well as Israelachvili,³⁵ have measured the shear viscosity of simple liquids and found that the shear flow is well described by bulk properties down to film thicknesses of several molecular diameters. In thinner films there is an apparent steady enhancement of viscosity which cannot be explained by the Reynolds theory of hydrodynamic lubrication.

When compressed polymer layers are subjected to tangential forces, as shown in Fig. 3, further rearrangement of the molecules in the direction of shear occurs. The response to stress appears to differ depending on the ability of the molecules to orient and align in the direction of force. Chains with smooth molecular profiles, such as the type Z molecules, are easier to stretch tending to increase their dimensions parallel to and decrease their size normal to the surface. This effect is clearly evident in Fig. 3, where with increasing load, the film thickness decreases from the static value of 9 nm to the dynamic value of 2.6 nm at high loads. It is interesting to note that sliding takes place at discrete separations, 3.4 and 2.6 nm, with the difference corresponding to the mean segmental diameter of the Z molecule. Thus, it is conceivable that the thinning process in this thickness regime proceeds by a stepwise squeezing of ordered molecularly thin layers of polymers similar to the shear induced layering previously observed with simple liquids.¹⁴⁻¹⁷ This is the first time that the structural effect has been observed in shear with long-chain molecules, which by virtue of their chain length can be partitioned between adjacent layers.

The shear behavior of polymer Y is quite different. The film resists thinning to a larger degree and the stepwise thinning pattern, as observed with polymer Z, is absent (Fig. 3). This is not surprising since the presence of the side groups is expected to interfere, presumably by an interlocking mechanism, with the ability of the chains to slip over each other, thus hindering their alignment in the shear field. From the lubrication point of view, the resistance to thinning is a very desirable property which allows for larger separations between sliding surfaces, lower friction, and reduction in wear.

In contrast to the previous experiment (Fig. 3), where the film thickness was measured as a function of load, the results presented in Fig. 4 were obtained at a fixed load and constant film thickness (within experimental error). The observed decrease in the shear stress with shear rate for polymer Z implies a "negative viscosity" which is difficult to reconcile in view of the rheological behavior of typical Newtonian and pseudoplastic liquids. For example, with

polymer melts such as PDMS, the materials appear less viscous at high rates of shear than at low rates.¹³ An acceptable explanation backed by spectroscopic data is that with the increasing shear rate a degree of alignment and elongation in the direction of shear reduces chain entanglement and interpenetration thus facilitating intermolecular sliding and lower friction.

The situation is quite different in our case where the molecules interact not only with each other but also with the mica substrates. With the film thickness at 2.6 nm, the surfaces are separated essentially by one or two monolayers of polymer chains stretched in the direction of sliding. Shearing is accomplished by the progressive breakage and formation of van der Waals bonds between the polymer segments and the surface and between weakly interacting molecules within the film. In other words, the surface-modified, molecularly thin films cease to behave as a polymer melt and acquire properties akin to solid films.

With solid films, as with polymer melts, there is a fairly direct influence of molecular structure on frictional behavior. In experiments involving simple liquids,¹⁴⁻¹⁷ the shear stress is reported to increase with decreasing number of molecular layers separating the surfaces. It was also found that the shear stress is independent of the sliding velocity when the surfaces are separated by a discrete number of layers, or when the film thickness is constant. This is consistent with the frictional behavior of typical boundary lubricants where molecularly thin films, usually of a low molecular weight, are chemisorbed or strongly physisorbed on the surface. In these systems, the frictional force is thought to be due to a physical lifting of the surfaces during translation^{15,36} and to the interaction energy barrier encountered when moving one surface from one equilibrium position to the next. Effects derived from the shear-induced orientability of the molecules are negligible due to compact shape of the molecules and their correspondingly fast relaxation times. However, there are examples where the resistance to shear is reported to decrease with the sliding velocity.^{4,5} In those systems [polytetrafluoroethylene (PTFE) and high density polyethylenes], the shear induced alignment of polymeric chains was clearly demonstrated to be responsible for the lower friction. Our results with polymer Z (Fig. 4) show a similar response to strain and suggest that molecular alignment is a dominant factor governing the frictional behavior of thin films. Note that the thickness of the film and the load were constant during sliding.

The presence of the side groups is more likely to disrupt the alignment process⁷⁻¹² and prevent the film from reaching the consistency of a solid film. It appears that the molecules are less restricted in their configurations and exhibit more freedom to slide past each other resulting in lower shear stresses and Newtonian-like flow behavior (Fig. 4). The 1:1 mixture of Z and Y polymers show intermediate response with little or no dependence of the shear stress on shear rate. This again is consistent with the notion that the presence of the side groups along the poly-

meric chain inhibits molecular ordering and hinders the transition from liquid to solid-like film.

During the sliding, chains are stretched in the direction of motion. The energy required for their deformation is balanced by the shear force. When stress is relieved, molecular alignment changes with time as the chains try to assume lower energy configurations. Figure 5 illustrates the relaxation process occurring in molecularly thin films. It is believed that at the instant the stress is applied and sliding commences, the random polymer orientation is disturbed and the chains begin to deform and stretch in the direction of shear. These changes in the molecular structure increase the potential energy of the molecules and are the source of the elastic force. New molecular arrangement no longer corresponds to the minimum energy configuration, and the elastic energy is balanced by the shear force. During a pause in sliding, the elastic force tries to bring the molecules back to a state of lower energy and less order. The longer the pause, the more time is available for the system to become disordered, and the higher is the static friction when sliding starts again. The difference between the static and kinetic friction decreases as the orientability of the film is reduced by increasing the fraction of molecules with side groups attached to the polymer backbone.

VI. CONCLUSIONS

These measurements have shown that the unique rheology of molecularly thin polymeric films translates into a lubricating behavior that is different from that of the bulk fluids in its dependence on velocity and load. Linear and molecularly smooth chains tend to align when subjected to shear and exhibit frictional properties akin to solidlike films. The side-chained molecules resist structuring and retain some fluidlike characteristics. In order to understand the lubricating behavior of the linear and branched polymers, it will be necessary to investigate the structure of the films during sliding, to ascertain that the molecules are in the aligned state as we assume. Finally, we want to emphasize that the characterization of polymer shear at the molecular level is necessary to understand and interpret frictional properties of lubricants and to establish an appropriate molecular-level model.

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